

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

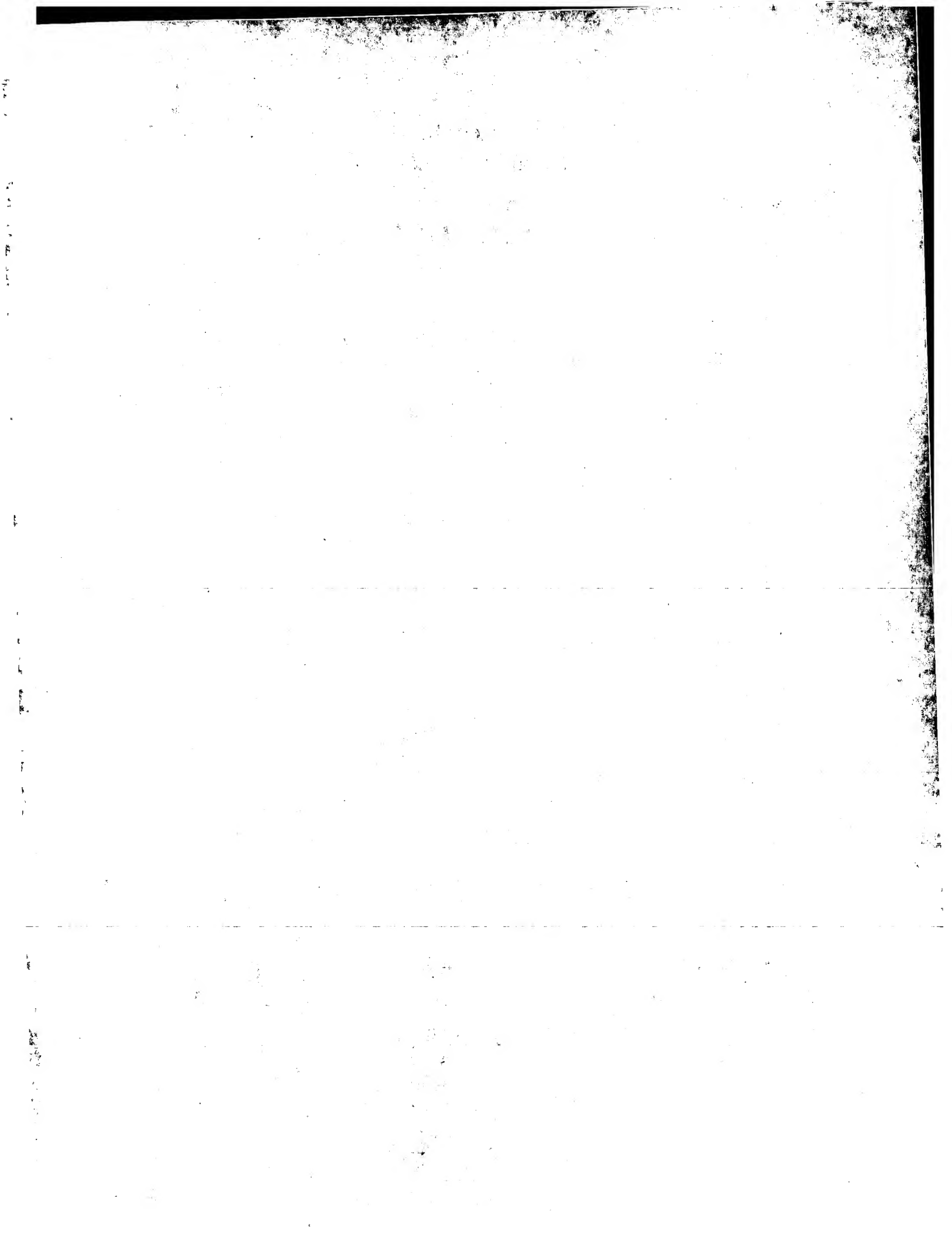
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



20

(12) **UK Patent Application** (19) **GB** (11) **2 167 867 A**

(43) Application published 4 Jun 1986

(21) Application No 8527305

(22) Date of filing 6 Nov 1985

(30) Priority data

(31) 8430318

(32) 30 Nov 1984

(33) GB

(71) Applicant

National Research Development Corporation (United Kingdom),
101 Newington Causeway, London SE1 6BU

(72) Inventors

Derek John Fray
Pei-Chih Yao

(74) Agent and/or Address for Service

P W Neville,
Patent Department, National Research Development Corporation, 101 Newington Causeway, London SE1 6BU

(51) INT CL⁴

G01N 27/56

(52) Domestic classification (Edition H):

G1N 19F1A 19LM 25B 25C4D 25DX BEJ
U1S 1453 1468 1469 G1N

(56) Documents cited

None

(58) Field of search

G1A

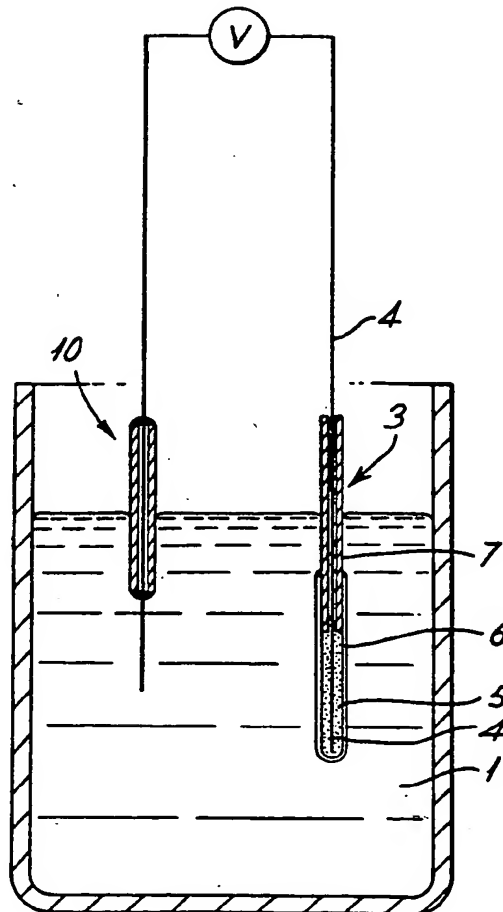
Selected US specifications from IPC sub-class G01N

(54) **Probe for determining lithium content**

(57) The probe, for use in a molten metal such as aluminium comprises a solid electrolyte for lithium ions 6 separating the molten metal from a lithium reference material 5 which is lithium ferrite and/or eutectoidally decomposed lithium titanate.

The solid electrolyte may be a lithium orthosilicate containing more than 10 mole % lithium phosphate.

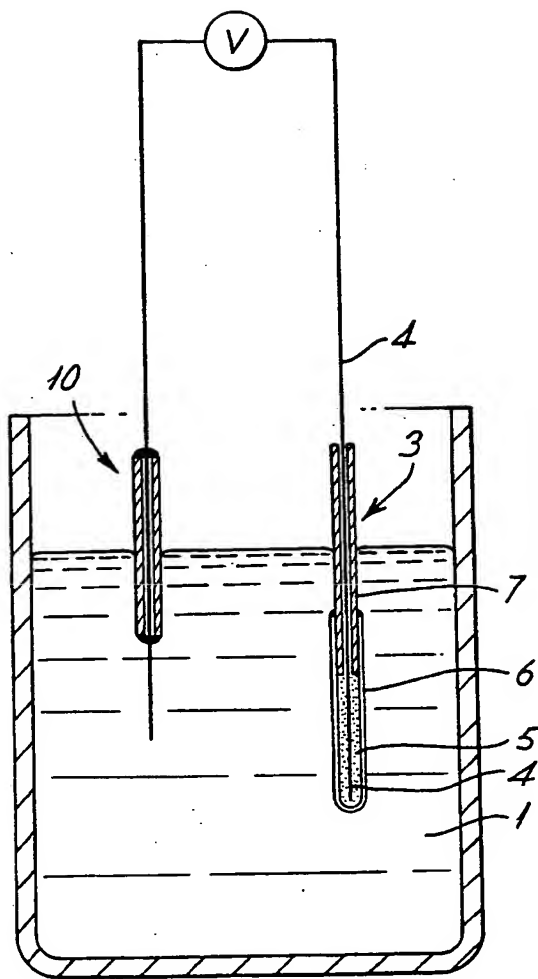
The reference may have a composition range $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to TiO_2 and may be in contact with air via protective tube 7 of α -alumina.



GB 2 167 867 A

2167867

1/1



SPECIFICATION

Probe for determining lithium content

- 5 This invention relates to a probe for determining the lithium content of a substance such as molten metals, especially aluminium.

During commercial smelting of aluminium in Hall-Heroult cells, lithium salts are added to the cells to raise the conductivity of the electrolyte and thereby reduce power consumption. Lithium, even in low quantities, however, drastically alters the casting properties of molten aluminium and the surface finish of some alloys. It is thus highly desirable to be able to determine quickly and simply the lithium content of molten aluminium. Another application would be in the control of Al-3% Li alloys.

The specification of our UK Patent No. 1,470,558 describes a method and apparatus for detecting and determining elements in the presence of other materials based on a galvanic method using β -alumina solid electrolyte probes. In this prior specification, it is proposed that a lithium β -alumina probe may be used for the determination and detection of lithium. Lithium β -alumina, however, is not wholly suitable for use in the construction of such a probe due to its brittle nature. In addition, at the elevated temperatures of molten metals, lithium β -alumina is liable to revert to sodium β -alumina in the presence of the sodium which always occurs in molten aluminium from aluminium smelting sources.

Our Patent GB-B-2025626 describes a solid electrolyte probe which is particularly suitable for use for the determination of lithium in the presence of molten metals or alloys, and which does not suffer from the deficiencies of the lithium β -alumina solid electrolyte material.

That probe monitors the e.m.f. generated between a substance and a reference material containing lithium, the substance and reference being separated from one another by a solid electrolyte which is electrically conductive to lithium ions, in which the probe is adapted to contain the reference material and to separate the reference material from the substance when the probe is introduced thereto, and in which the solid electrolyte comprises β -spodumene. β -spodumene is a compound comprising a $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2$ mixture and having a wide range of compositions but typically $\text{Li}_2\text{O}.\text{Al}_2\text{O}_3.4\text{SiO}_2$.

The reference material disclosed in that patent is a three-phase solid material comprising β -spodumene, in one example, a mixture of β -spodumene/ $\text{Li}_2\text{O}.\text{SiO}_2/\text{Li}_2\text{O}.2\text{SiO}_2$.

The present invention is a probe for determining the lithium content of a substance by monitoring the e.m.f. generated between the substance and a reference material containing lithium, the probe comprising, exposable to the substance, a solid electrolyte for lithium ions, and, separated by the solid electrolyte

from the substance, a lithium reference material comprising lithium ferrite and/or eutectoidally decomposed lithium titanate.

The reference material may be within the composition range $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to TiO_2 . Preferably (to keep its oxygen activity constant) air can reach the reference material.

The probe is conveniently in the form of a tube of the electrolyte containing the reference material.

The solid electrolyte may be a lithium orthosilicate containing more than 10 mole % lithium phosphate. The probe may further comprise an electronically conducting internal electrode contacting the reference material and not the electrolyte.

The present invention also extends to a method of determining the lithium content of a substance, comprising monitoring the e.m.f. generated between the substance and the reference material of a probe as set forth above. Usually, the substance in question will be molten aluminium (or aluminium alloy).

The invention will now be described by way of example with reference to the accompanying drawing, which shows a probe according to the invention in use for measuring lithium in molten aluminium.

A crucible contains molten aluminium 1 containing an unknown proportion of lithium.

A probe 3 according to the invention has a stainless steel wire 4 surrounded by tightly packed reference material 5 having a stable lithium activity. This material 5, in turn, is enclosed in a tube of solid electrolyte 6 closed at its bottom and, at its top, sealed into an inert upward extension protective tube 7 of α -alumina which permits air to circulate over the reference material 5. The tube of electrolyte 6 has an internal diameter of about 5 mm and a wall thickness of about 1 mm. The probe 3 is dipped into the crucible of molten aluminium 1, but the tubes 6 and 7 prevent the aluminium 1 from contacting the wire 4.

A counterelectrode 10 consists of a stainless steel wire with some suitable inert gripper (for example of α -alumina) and is dipped in the molten aluminium 1. The probe 3 and the counterelectrode 10 are connected to opposite sides of a high-impedance voltmeter V.

This assembly is an electrochemical cell, thus:

$\text{Li reference } 5 | \text{Li}^+ \text{ electrolyte } 6 | \text{Al} + \text{Li } 1.$

The potential measured across this cell is a measure of the lithium activity in the molten aluminium 1, being proportional to $T \ln$

(lithium activity in 5)

(lithium activity in 1)

where T is the temperature.

(The temperature is measured by a thermocouple, not shown, immersed in the molten aluminium 1).

The reference material 5 must be suitably chosen, and will be complemented by a suitably chosen electrolyte 6.

Considering first the reference material 5, this should clearly have a stable lithium activity. However it should also reach equilibrium quickly at a given temperature, and ideally it should be both an ionic and electronic conductor. The phase diagram of the $\text{Li}_2\text{O}-\text{TiO}_2$ system is well defined and in the two-phase region $\text{Li}_4\text{Ti}_5\text{O}_{12} + \text{TiO}_2$, the lithium oxide activity remains constant. If the oxygen partial pressure is then fixed by either exposing the reference to air or a copper-copper oxide mixture, the lithium activity is also fixed. Such a material also has an electronic conductivity near to that of a semi-metal. It was prepared as follows: Polycrystalline $\text{Li}_2\text{Ti}_3\text{O}_7$ powder was prepared from rutile and lithium carbonate, mixed in the appropriate ratios, fired at 1073 K to decompose the carbonate, reground, fired at 1473 K and air quenched. When the resulting ramsdellite-like $\text{Li}_2\text{Ti}_3\text{O}_7$ phase was held just below 1213 K, it decomposed eutectoidally to form rutile and $\text{Li}_4\text{Ti}_5\text{O}_{12}$. When compressed into the tube 6, this material 5 was allowed free access to atmospheric air to provide a consistent oxygen partial pressure over it, to fix its lithium activity as explained.

Turning to the solid electrolyte 6, there is a choice of known lithium-ion conductors. However, the molten aluminium 1 is likely to contain not only lithium but also sodium; thus the electrolyte 6 should be stable in aluminium and not readily interchange with sodium. Lithium orthosilicate is a good lithium ion conductor at temperature higher than 673 K and the conductivity can be enhanced by three orders of magnitude by adding 40 mole % lithium orthophosphate. At higher temperatures, lithium orthosilicate (Li_4SiO_4) is characterised by a disordered cation lattice with eight lithium ions distributed over 18 sites. The addition of lithium phosphate (Li_3PO_4) introduces interstitial lithium sites which contribute to the overall conductivity. The overall structure of the solid solution can be regarded as silicate and phosphate tetrahedra linked together by a large number of lithium sites. The addition of more than 10 mole % Li_3PO_4 leads to a two-phase mixture, which is said to be stable in the presence of molten lithium. The solid electrolyte 6 selected for making probes 3 had the overall composition $\text{Li}_{3.6}\text{Si}_{0.6}\text{P}_{0.4}\text{O}_4$.

$\text{Li}_{3.6}\text{Si}_{0.6}\text{P}_{0.4}\text{O}_4$ powder was prepared by calcining the appropriate mixture of lithium orthosilicate Li_4SiO_4 and lithium phosphate Li_3PO_4 in an alumina crucible at 1173 K, the lithium orthosilicate having been prepared by solid state reaction between Li_2CO_3 and SiO_2 at 1073K. The powder was ball-milled, and tubes 6 formed by isostatic pressing at 60 kN cm² and sintering in air at 1173 K for two hours followed by surface cooling. Overfiring can lead to unsatisfactory products. All starting

materials and the various stages of preparation were routinely checked for completeness of reaction by X-ray powder diffraction.

The sintered tubes 6 were examined by scanning electron microscopy and by a qualitative leak test; any having open pores or admitting air when evacuated were rejected.

Examination of an assembled probe 3 after some use showed that the reference material 5 sinters to the tube of electrolyte 6. The tube electrolyte 6 was not attacked after extended immersion in the molten aluminium, but we found some reaction between the tube and molten lithium and also between the tube and humid air.

On placing the probes in lithium-free aluminium, a potential of around 0.6 V was attained at 993 K. The addition of lithium alloy to the melt caused the voltage to increase over three minutes to a sharply defined maximum of about 1 V, which then gradually began to decline to the original 0.6 V over several hours, presumably as the lithium oxidised away. The potential E was found to be related to X, the mole % lithium, approximately as follows:

$$\text{At } 984 \text{ K, } E = 0.0728 \ln X + 1.552$$

$$\text{At } 1050 \text{ K, } E = 0.0907 \ln X + 1.706$$

The theoretical Nernst slopes are 0.0847 and 0.0905 respectively. In dilute alloys, Henry's law is obeyed.

100 CLAIMS

1. A probe for determining the lithium content of a substance by monitoring the e.m.f. generated between the substance and a reference material containing lithium, the probe comprising, exposable to the substance, a solid electrolyte for lithium ions, and, separated by the solid electrolyte from the substance, a lithium reference material comprising lithium ferrite and/or eutectoidally decomposed lithium titanate.

2. A probe according to Claim 1, wherein the reference material is within the composition range $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to TiO_2 .

3. A probe according to Claim 1 or 2, wherein air can reach the reference material.

4. A probe according to any preceding claim, in the form of a tube of the electrolyte containing the reference material.

5. A probe according to any preceding claim, wherein the solid electrolyte is a lithium orthosilicate containing more than 10 mole % lithium phosphate.

6. A probe according to any preceding claim, further comprising an electronically conducting internal electrode contacting the reference material and not the electrolyte.

7. A probe according to Claim 1, substantially as hereinbefore described.

8. A method of determining the lithium content of a substance, comprising monitoring

the e.m.f. generated between the substance and the reference material of a probe according to any preceding claim.

9. A method according to Claim 8, wherein
5 said substance is molten aluminium or a molten aluminium alloy.

Printed in the United Kingdom for
Her Majesty's Stationery Office, Dd 8818935, 1986, 4235.
Published at The Patent Office, 25 Southampton Buildings,
London, WC2A 1AY, from which copies may be obtained.

